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(54) EPOXY RESIN COMPOSITIONS CONTAINING AROMATIC DISULFONAMIDE SALTS

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ABSTRACT

This invention concerns compositions containing an epoxy resin having an average of more than one 1,2-epoxy group per molecule, an aromatic disulfonamide as latent curing agent, and an accelerator selected from phosphonium salts, imidazoles, ammonium salts, alkali metal hydroxides, and salts of aromatic disulfonamides with tertiary amines, or hydrocarbon substituted phosphines. The compositions are useful in such applications as coatings, adhesives, castings, or laminates.

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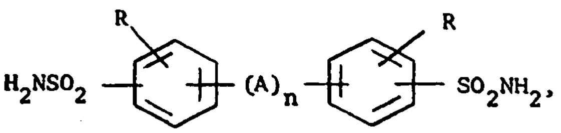
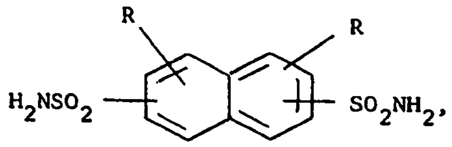
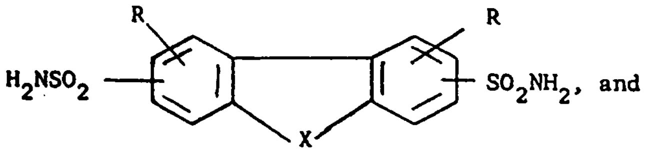
This invention concerns epoxy resin compositions containing a latent curing agent.

Dicyandiamide is commonly employed as a latent curing agent in epoxy resin compositions. These compositions produce coatings that have a hazy or grainy appearance. Furthermore, the compositions of the prior art which contain liquid epoxy resins and dicyandiamide are latent for periods of only about a week and in some instances possibly up to about a month before the composition gells, probably due to catalytic action of the dicyandiamide causing an epoxy-to-epoxy reaction.

The present invention provides a composition comprising (1) an epoxy resin containing an average of more than one 1,2-epoxy group per molecule, (2) an aromatic disulfonamide as latent curing agent, and (3) an accelerator selected from phosphonium salts, imidazoles, ammonium salts, alkali metal hydroxides, and salts of aromatic disulfonamides with tertiary amines or hydrocarbon substituted phosphines, wherein the components are present in an amount to provide an amine hydrogen: epoxy equivalent ratio of at least 0.9:1, and the aromatic disulfonamide corresponds to one of the formulae







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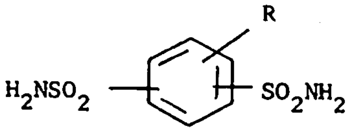


wherein A is a divalent hydrocarbon group having from 1 to 6 carbon atoms, -O-, -SO-, $-SO_2-$, -S-S-, or a single bond; each R is hydrogen, an aliphatic hydrocarbon group having from 1 to 6 carbon atoms, Cl, Br, or alkoxy having from 1 to 6 carbon atoms; n is 0 or 1; and X is O or S.

The compositions of this invention are useful in such applications as coatings, adhesives, castings, or laminates, and may also contain one or more additives such as, for example, flow control agents, pigments, solvents, dispersing agents, or fire retardants.

The compositions of the invention have improved latency, being stable at ambient temperatures for periods up to six months or longer. The compositions produce coatings having improved appearance in that such coatings are not hazy or grainy, but are glossy and smooth.

Disulfonamides such as represented by the above formulae include, for example, diphenylether-4,4'-disulfonamide, di(bromophenyl)ether-4,4'-disulfonamide, di(methylphenyl)ether-4,4'-disulfonamide, di(butylphenyl)ether-4,4'-disulfonamide, di(propylphenyl)ether-4,4'-disulfonamide, di(chlorophenyl) ether-4,4'-disulfonamide, naphthalene-1,5-disulfonamide, methyl-naphthalene-1,5-disulfonamide, ethyl-naphthalene-1,5-disulfonamide, dipropylnaphthalene-1,5-disulfonamide, chloronaphthalene-1,5-disulfonamide, bromo-naphthalene-1,5-disulfonamide, dibromonaphthalene-1,5-disulfonamide, meta- and para-phenylene disulfonamide, dibenzofuran disulfonamide, dibenzothiophene disulfonamide, and mixtures thereof.

The disulfonamides conveniently can be prepared by chlorosulfonating the desired aromatic compound with at least a stoichiometric quantity of a suitable chlorosulfonation agent such as, for example, chlorosulfonic acid at a temperature of from 50°C. to reflux temperature for from 2 to 6 hours or longer. The resultant disulfonyl chloride after removal of any excess chlorosulfonation agent is then reacted with aqueous or anhydrous ammonia at 40-150°C. under the autogenous pressure of the ammonia for 2 to 24 hours. The resultant disulfonamide is then precipitated in cold water, filtered, and the product is finally recovered by slurrying the precipitate in hot water and again filtering.

The salt of an aromatic disulfonamide with a tertiary amine or hydrocarbon substituted amine, when used, is normally employed in an amount greater than 1.0 weight percent and preferably from 5.0 to 100 weight percent based on the weight of the aromatic disulfonamide.

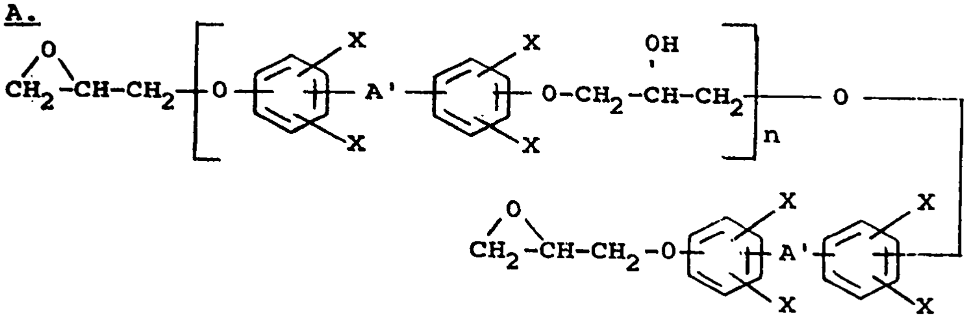
The anionic moieties of the salts of aromatic disulfonamides are tertiary amines such as 2-methylimidazole, dimethyl aniline, triethylenediamine, hexamethylene tetramine, triethylamine, or triethanolamine, or hydrocarbon substituted phosphines such as triaryl phosphines such as triphenyl phosphine or trialkyl phosphines such as trimethyl phosphine or triethyl phosphine.

The disulfonamide salts can be prepared by dissolving the disulfonamide and the amine or phosphine in a ketonic solvent and then removing the solvent to obtain the salt so produced.

Suitable accelerators also include phosphonium compounds, such as, for example, ethyltriphenylphosphonium acetate·acetic acid complex; imidazoles, such as, for example, 2-methyl imidazole; ammonium salts, such as, for example, benzyltrimethyl ammonium chloride; alkali metal hydroxides, such as, for example, sodium hydroxide; and mixtures thereof. Suitable phosphonium compounds which may be employed as accelerators include those phosphonium salts of an inorganic acid and salts of organic acids, esters and acid-esters. Such phosphonium compounds are more fully described in French Patent 2,093,785 and U.S. Patents 3,477,990 and 3,341,580. These accelerators are usually employed in quantities of from 0.1 to 5.0 and preferably from 0.5 to 1.0 parts by weight based upon total resin solids, i.e. epoxy plus aromatic disulfonamide.

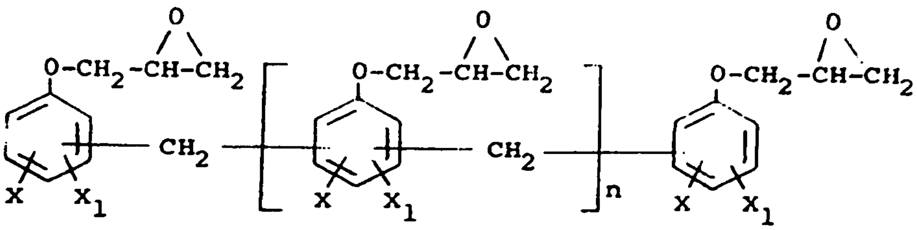
Suitable epoxy resins for use in this invention have an average of more than one 1,2-epoxy group per molecule. These include, for example, those epoxy resins represented by the following general formulae:

A.



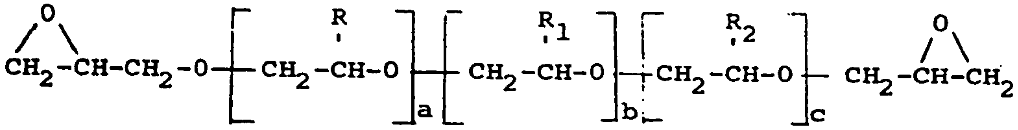
wherein each A' is a divalent hydrocarbon group having from 1 to 4 carbon atoms, -S-, -S-S-, $-SO_2-$, -SO-, -CO-, or -O-, X is hydrogen or a halogen and n is an integer having an average value of from 0 to 10;

B.



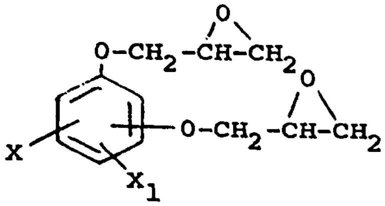
wherein X and X_1 each is hydrogen, an alkyl group having from 1 to 4 carbon atoms, or halogen, and n is an integer having an average value of from 0.1 to 4;

C.



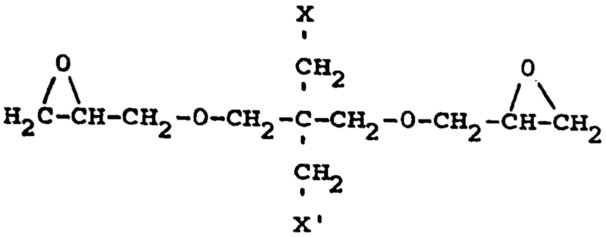
wherein R, R_1 and R_2 each is hydrogen, an alkyl or haloalkyl group having from 1 to 4 carbon atoms, and a, b and c are integers, the sum of which is an integer having an average value of from 3 to 40;

D.



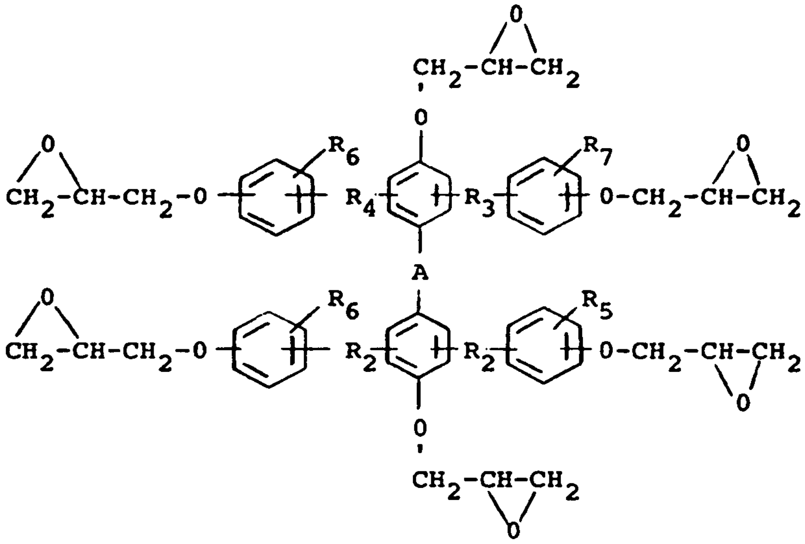
wherein X and X_1 are as indicated in formula B above.

E.



wherein X and X' each is hydrogen, chlorine, or bromine.

F.



wherein A is a divalent radical selected from alkylidene, cycloalkylidene, -S-, -S-S-, $-SO_2-$, -SO-, -CO-, and -O-; R_1, R_2, R_3 and R_4 are the same or different alkylidene groups; and R_5, R_6, R_7 and R_8 are independently halogen, hydrogen or alkyl groups having from 1 to 4 carbon atoms.

The following examples are illustrative of this invention.

EXAMPLES 1-3

Coating solutions were prepared as in Table I from an epoxy resin employing diphenyl ether disulfonamide (DPODSA) as the latent curing agent and also containing 2-methylimidazole or a salt of DPODSA with 2-methylimidazole (2-MI). The coating compositions were applied to cold rolled steel panels at a coating thickness of about 0.5 mil. (12.7 microns), cured and tested as indicated in Table II.

The Hot Tack Test is an indication of curing. A wooden tongue depressor was drawn across the hot coating surface and if the coating was marked, a lack of cure was indicated. If it was not marked, then the coating was deemed to have cured. In the Table, a "yes" indicates that the coating was marked by the tongue depressor while a "no" indicates that the coating was not marked.

The impact test is carried out using a four pound (1.8 kg.) dart having a one-inch (2.5 cm.) ball on its tip which is dropped from various heights onto the backside of the panel. Impact (weight of dart times the height of drop) distorts the panel and coating into a cavity and indicates coating toughness. Pass means no fracture or flaking of the coating. Fail means the opposite.

MEK test is a solvent resistance spot test wherein a piece of paper toweling is saturated with methyl ethyl ketone, placed on the coating and covered with a watch glass for 3 minutes. The glass and towel are removed by wiping and the effect on the coating is observed.

TABLE I

Coating Formulations

	Ex. 1	Ex. 2	Ex. 3
Epoxy Resin*	69.8 g. (0.367 eq.)	69.8 g.	69.8 g.
DPODSA	30.2 g. (0.368 eq.)	28.2 g.	26.2 g.
2-MI	1.2 g.	--	--
1/1 2-MI - DPODSA Salt**	--	2.5 g.	5.0 g.
2-Methoxyethanol	100.0 g.	100.0 g.	100.0 g.
% Catalyst (Based on Solids)	1.2	0.5	1.0

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* Diglycidyl ether of Bisphenol A having an epoxy equivalent weight of about 190

** 1/1 Mole ratio mixture of 2-MI and free DPODSA

TABLE II

Results of Oven Cures of Epoxy Coating Formulations

Formulation	Ex. 1	Ex. 2	Ex. 3
350°F. (177°C. Cures			
15 Minutes			
Hot Tack	No	No	No
180 kg.-cm. Impact	Pass	Pass	Pass
MEK Spot Test (3 Min.)	~No effect	~No effect	~No effect
300°F. (149°C.) Cures			
15 Minutes			
Hot Tack	--	No	--
180 kg.-cm. Impact	--	Pass	--
MEK Spot Test (3 Min.)	--	Softens	--
30 Minutes			
Hot Tack	--	No	--
180 kg.-cm. Impact	--	Pass	--
MEK Test (3 Min.)	--	No effect	--
60 Minutes			
Hot Tack	--	No	--
180 kg. -cm. Impact	--	Pass	--
MEK Test (3 Min.)	--	No effect	--

EXAMPLES 4 and 5

Examples 2 and 3 were repeated using 40 gms. of toluene in place of the 100 gms. of 2-methoxyethanol. These compositions had a shelf life of over nine months.

A similar composition containing one equivalent of dicyandiamide per epoxy equivalent and 0.5% by weight 2-methylimidazole had a shelf life of about one week.

EXAMPLES 6-10

The procedures of Examples 1-3 were repeated using various salts. The coating formulations are given in Table III.

TABLE III

Example	6	7	8	9	10
Epoxy Resin*, g.	95	95	95	95	95
DPODSA, g.	2.39	4.73	6.28	4.3	6.0
Salt**, g.	9.14	6.80	5.25	7.3	5.8
2-Methoxyethanol, g.	170	170	170	170	170
Coating Evaluation					
Minimum time to absence of hot tack, min.	10	10	45	>30	10
180 kg.-cm. Impact	Pass	Pass	Pass	Pass	Pass
Cure time to Resist Solvent (1 min. MEK Spot Test), Min.	15	10	>45	>30	10

*Diglycidyl ether of bisphenol A having an epoxy equivalent weight of about 775.

**Salt

Example	Mole Ratio DPODSA:Amine	Amine
6	4:1	2-Methylimidazole
7	4:1	Triethylenediamine
8	3.5:1	Triethanolamine
9	6.5:1	Triethylamine
10	3.5:1	Hexamethylenetetramine

EXAMPLE 11

Solution coatings were prepared from an epoxy resin employing diphenyl ether disulfonamide as the latent curing agent and also containing 2-methyl imidazole or a phosphonium compound as an accelerator. The compositions of the coatings and the properties are given in Table IV. The coating compositions were applied to cold rolled steel panels at a coating thickness of about 1 mil (25 microns) and cured as indicated in Table IV.

TABLE IV

Composition and Property	Coating A	Coating B	Coating C
Epoxy Resin,[1] g.	9.5	9.5	9.5
2-Methyl imidazole, g.	0	0	0.05
Diphenylether disulfonamide, g.	1.0	1.0	1.10
Phosphonium compound,[2] g.	0.05	0.1	0
Diacetone alcohol, g.	23	23	23
Cured at 175°C for the Indicated Time			
5-Minute Cure			
Film Appearance	Very good	Very good	Very good
Hot Tack	yes	no	no
180 kg.-cm. Impact	fails	pass	pass
Acetone Spot Test	fails	softens	softens slightly
10-Minute Cure			
Film Appearance	very good	very good	very good
Hot Tack	very slight	no	no
180 kg.-cm. Impact	pass	pass	pass
Acetone Spot Test	softens	softens	softens slightly
15-Minute Cure			
Film Appearance	very good	very good	very good
Hot Tack	no	no	no
180 kg.-cm. Impact	pass	pass	pass
Acetone Spot Test	softens	softens	softens slightly
30-Minute Cure (Overcure)			
Film Appearance	very good	very good	very good
Hot Tack	no	no	no
180 kg.-cm. Impact	pass	pass	pass
Acetone Spot Test	softens	softens	softens slightly

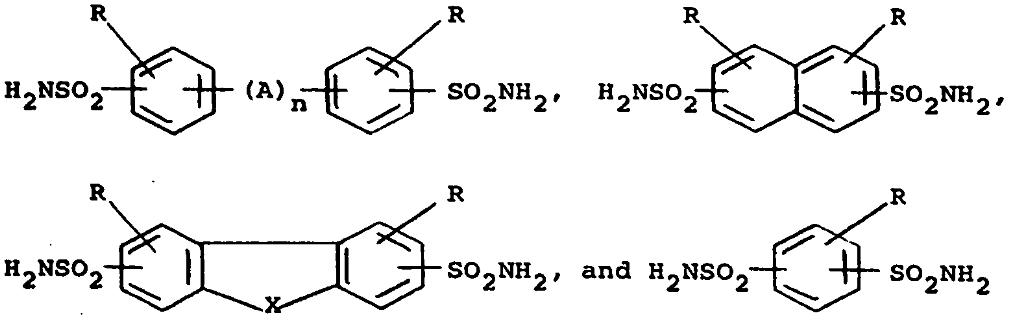
Footnote to Table IV

[1] The epoxy resin was a diglycidyl ether of bisphenol A having an EEW of about 700-875.

[2] The phosphonium compound was ethyltriphenyl phosphonium acetate·acetic acid complex.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A composition comprising (1) an epoxy resin containing an average of more than one 1,2-epoxy group per molecule, (2) an aromatic disulfonamide as latent curing agent, and (3) an accelerator selected from phosphonium salts, imidazoles, ammonium salts, alkali metal hydroxides, and salts of aromatic disulfonamides with tertiary amines or hydrocarbon substituted phosphines, wherein the components are present in an amount to provide an amine hydrogen: epoxy equivalent ratio of at least 0.9:1, and the aromatic disulfonamide corresponds to one of the formulae



wherein A is a divalent hydrocarbon group having from 1 to 6 carbon atoms, -O-, -SO-, $-SO_2-$, -S-S-, or a single bond; each R is hydrogen, an aliphatic hydrocarbon group having from 1 to 6 carbon atoms, Cl, Br, or alkoxy having from 1 to 6 carbon atoms; n is 0 or 1; and X is O or S.

2. A composition according to Claim 1 wherein the amine hydrogen:epoxy equivalent ratio is from 0.9:1 to 1.25:1.

3. A composition according to Claim 1 which contains a salt of an aromatic disulfonamide with a tertiary amine or hydrocarbon substituted phosphine in an amount of

from 5.0 to 100 weight percent based on the weight of the aromatic disulfonamide.

4. A composition according to Claim 3 wherein the tertiary amine is 2-methylimidazole, N,N-dimethylaniline, triethylenediamine, hexamethylenetetramine, triethylamine, or triethanolamine.

5. A composition according to Claim 3 wherein the hydrocarbon substituted tertiary phosphine is a triaryl phosphine or a trialkylphosphine.

6. A composition according to Claim 1 which contains an accelerator selected from phosphonium salts, imidazoles, ammonium salts, and alkali metal hydroxides in an amount of from 0.1 to 5.0 weight percent based on the combined weight of the epoxy resin and aromatic disulfonamide.

7. A composition according to Claim 6 which contains the accelerator in an amount of from 0.5 to 1.0 weight percent based on the combined weight of the epoxy resin and aromatic disulfonamide.

8. A composition according to Claim 6 or 7 wherein the accelerator is 2-methylimidazole, ethyltriphenylphosphonium acetate·acetic acid complex, or a salt of diphenylether disulfonamide with 2-methylimidazole, with triethylenediamine, with triethanolamine, with triethylamine, or with hexamethylenetetramine.

9. A composition according to Claim 1 wherein the aromatic disulfonamide is diphenylether disulfonamide.

10. A composition according to Claim 1 wherein the epoxy resin is a glycidyl ether of bisphenol A.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente